

# Progress Related to Mo-99 Separation, Precipitation Prevention, and Clean-Up for SHINE System

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# Potential Domestic Mo-99 Producer

- Morgridge Institute for Research (MIR) and SHINE Medical Technologies
- D/T-accelerator-driven process
- SHINE (Subcritical Hybrid Intense Neutron Emitter)
- LEU uranyl sulfate solution
- Titania sorbents to separate and recover Mo-99
- Catalyst required to prevent precipitation
- Sulfate-to-nitrate conversion followed by UREX for clean-up



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# Mo-99 Separation



- Titania (110  $\mu\text{m}$ ) for initial recovery column
- Titania (40  $\mu\text{m}$ ) for concentration column
- Solution and column kept at 80°C
- ~90 – 100% Mo recovery achieved when strip solution heated to 70°C and stripping velocity reduced

# Plant-Scale Column Designs

Column ID (cm)	Velocity (cm/min)	Column Length (cm)	Column Volume (L)	Sorbent Mass (kg)	$\Delta P$ (atm)	Mo-99 / Sorbent Mass (Ci/g)
10	27.8	20	1.6	2.04	0.63	1.90
12	19.3	14	1.6	2.06	0.30	1.89
15	12.4	9	1.6	2.07	0.13	1.88
20	7.0	5	1.6	2.04	0.04	1.90

- Designs assume 100 – 150 g-U/L, 200 – 250 L, 2 h loading time, Mo concentration  $\sim 10^{-6}$  M
- Feed loaded in **up-flow** direction
- Column washed **up-flow** with 5 – 10 CVs of acid and water
- Mo eluted **down-flow** with 20 – 30 CVs of 0.1 M NaOH at 70°C
- $\sim 22$  – 48 L of Mo-strip solution will be generated
- Concentration column will be added to decrease strip volume



# Strip Volume Minimization

- Titania sorbent (40  $\mu\text{m}$ ) will be used for the concentration column
- 0.1 M NaOH will be used to strip Mo from the initial recovery column
- Strip solution would be acidified using  $\text{HNO}_3$
- Langmuir parameters were determined for a pH 2 and pH 5 solution – much better adsorption at pH 2
- 1 M  $\text{NH}_4\text{OH}$  will be used to strip Mo from the concentration column
- Strip volume can be reduced to  $< 1 \text{ L}$



# Concentration column following a 2 h recovery of Mo from 130 g-U/L uranyl sulfate solution

## Plant-Scale Concentration Column Design

Sorbent	Target Mo loading (%)	Column ID (cm)	Velocity (cm/min)	MTZ <sub>0.1%</sub> (cm)	Column length (cm)	Column volume (mL)	Sorbent weight (g)	$\Delta P$ (atm)	Mo-99 / sorbent mass (Ci/g)	Strip volume (mL)
TiO <sub>2</sub>	99.9	4	31.2	1.1	1.5	19	24	0.32	163	377

## Process Conditions

Solution	NaNO <sub>3</sub> , pH 2
Mo concentration	2.34e-2 mM
Volume	23.52 L
loading time	60 min
flow rate	392 mL/min
loading temperature	80 °C
density	0.972 g/mL
viscosity	0.355 cp

## Down-Scale Results (0.66 cm ID x 1.5 cm L)

Stream	% Mo-99
Effluent	0.3
0.01 M HNO <sub>3</sub> Wash	0.01
H <sub>2</sub> O wash	0.03
1 M NH <sub>4</sub> OH strip	89



# Downscale Column Experiments at the VDG



- Direct down-scale column experiments of VERSE plant-design
- Solution irradiated prior to and during column loading
- 0.2 – 2 L uranyl sulfate solution heated to 80°C
- Mo found in effluent or not recovered in strip – Mo reduction
- N<sub>2</sub> purge to dilute H<sub>2</sub> and O<sub>2</sub> from water radiolysis

# VDG Column Results

Experiment Date	Solution Dose Rate (kRad/h)	Column Dose Rate (kRad/h)	% Mo in Effluent	%Mo in Washes	% Mo Recovered	Acid Wash
2/14/2013	64.3	15.5	0.9	0.3	100	0.5 M H <sub>2</sub> SO <sub>4</sub>
2/27/2013	74.1	17.8	0.7	15	92	1 M H <sub>2</sub> SO <sub>4</sub>
3/6/2013	67.8	16.3	0.6	11	100	1 M H <sub>2</sub> SO <sub>4</sub>
3/12/2013	68.8	16.6	0.2	2	95	0.5 M H <sub>2</sub> SO <sub>4</sub>

- Solution loaded onto column while under constant source of radiation
- Washes and elution performed using AKTA LC system
- No evidence of changes in Mo redox chemistry due to radiolysis at low dose rates (~70 kRad/h)
- Acid wash concentrations varied to remove Pu, which was added as a spike to some of the solutions





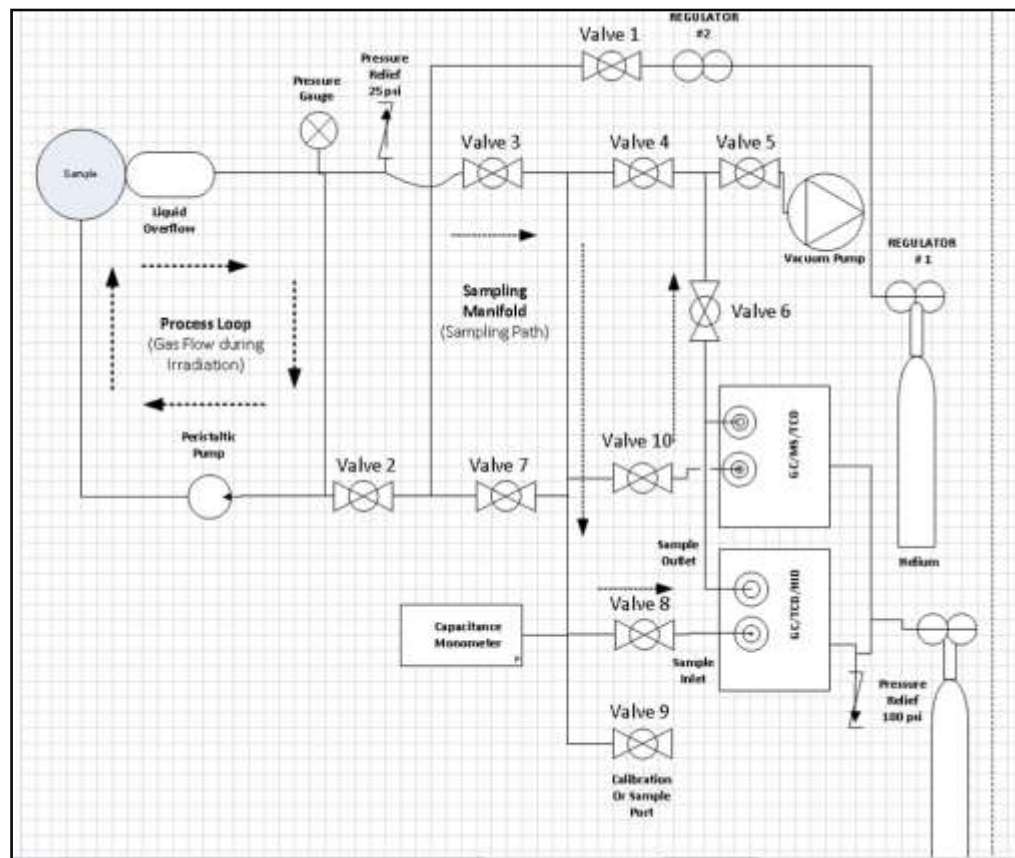
# Pu-239 Results from VDG Column Experiments

H <sub>2</sub> SO <sub>4</sub> (M)	% Pu-239 Effluent	% Pu-239 H <sub>2</sub> SO <sub>4</sub> Wash	% Pu-239 H <sub>2</sub> O Wash #1	% Pu-239 NaOH Strip	% Pu-239 H <sub>2</sub> O Wash #2	% Pu-239 on Column	% Mo in H <sub>2</sub> SO <sub>4</sub> Wash
0.5	12.2	9.6	3.0	22.6	0.3	52.3	0.1
1	19.4	58.8	10.4	1.9	0.5	9.0	8

- Column feed solutions spiked with Pu-239 before irradiation
- Samples analyzed via alpha spectroscopy
- Spent columns do not have to be GTCC waste if Pu kept low
- 0.5 M H<sub>2</sub>SO<sub>4</sub> left ~50% Pu on column
- 1 M H<sub>2</sub>SO<sub>4</sub> left <10% Pu on column
- 1 M H<sub>2</sub>SO<sub>4</sub> changed Mo chemistry....premature elution of Mo
- It becomes a balancing act – want to remove Pu but cannot afford to lose Mo product
- Finding optimum conditions is still underway
- Dose rates much less than what is expected for SHINE



# Radiolytic Gas Generation and Peroxide Catalysis Setup at VDG



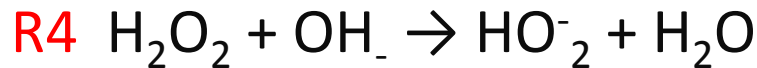
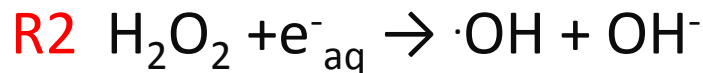
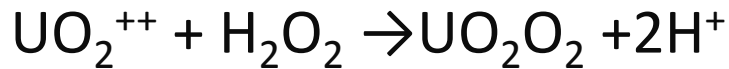
- Uranyl sulfate solutions irradiated for 5 h with dose rates of  $\sim 3400$  MRad/h
- Expected doses to SHINE solution – 1 h (360 Mrad) and 5 days (43,200 MRad)
- Dose applied to most solutions at VDG equivalent to  $\sim 2$  days of operation

# Precipitation in Uranyl Sulfate Samples



- Precipitate dissolved after solution was boiled for a few minutes
- 88 g-U/L went to 63.5 g-U/L final pH 0.64 after  $1.712\text{E}+08$  Gy (235 min)
- 298 g-U/L went to 262 g-U/L final pH 0.58 after  $2.033\text{E}+08$  Gy (270 min)
- Uranyl peroxide – not observed during irradiation of uranyl nitrate solutions exposed to same doses
- $\text{HNO}_2$  – by-product of nitrate radiolysis catalyzes  $\text{H}_2\text{O}_2$  destruction

# Peroxide Formation and Decomposition



## Thermal decomposition



## Known Catalytic decomposition by addition of metal salts

Fe, Cu, Ag, Ni, Mn, Ti, I, Cr

## Catalysts tested at Argonne using VDG

$\text{FeSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{CuSO}_4$ , KI, Zr, 304 stainless steel turnings



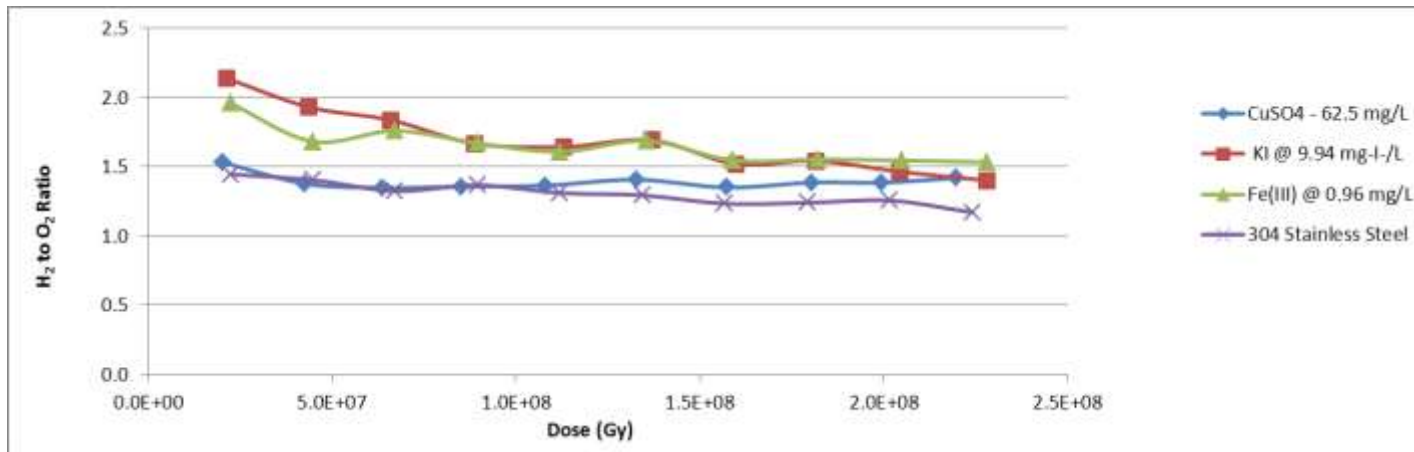
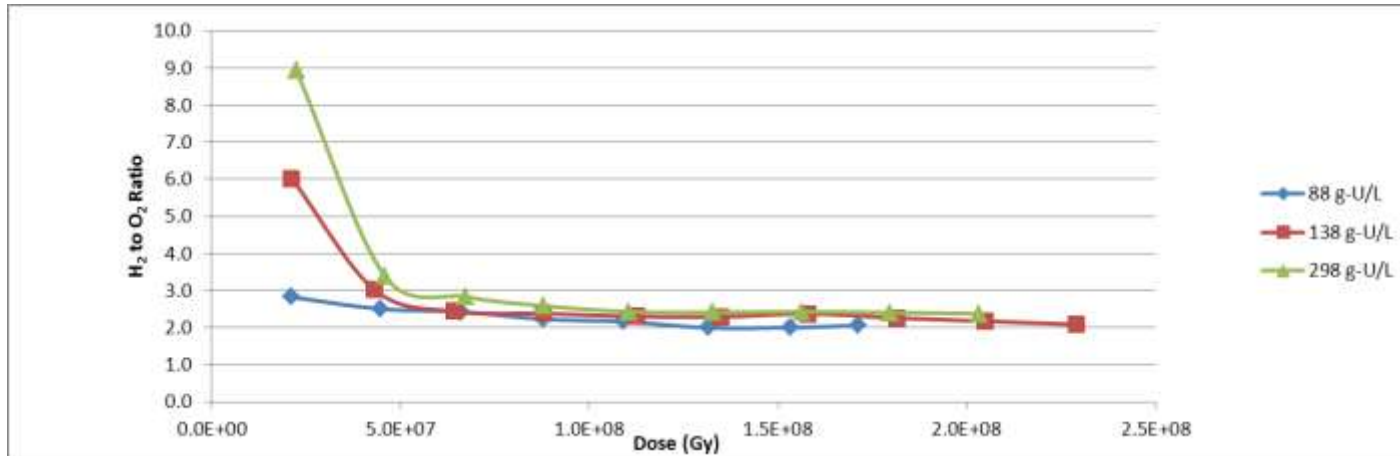
# Catalytic Destruction of Peroxide

Catalyst	UO <sub>2</sub> SO <sub>4</sub> (g-U/L)	Energy Deposited (MRad)	Precipitation	Initial pH	Final pH	μmoles H <sub>2</sub> Produced	μmoles O <sub>2</sub> Produced	H <sub>2</sub> to O <sub>2</sub> Ratio
0.99 mg/L FeSO <sub>4</sub>	124	23100	NO	1.4	N.A.	239	163	1.47
Cu(II), 62.5 mg-Cu/L	126	22000	NO	1.4	N.A.	406	286	1.42
KI, 9.94 mg-I-/L	126	22800	NO	1.4	N.A.	206	147	1.40
Fe(III) 0.96 mg/L	126	22800	NO	1.4	N.A.	566	369	1.53
304 Stainless Steel	126	22400	NO	1.4	N.A.	261	223	1.17
Zirconium Metal	298	23200	YES	1.0	N.A.	1112	460	2.42

- All catalysts prevented precipitation of uranyl peroxide except Zr
- H<sub>2</sub> to O<sub>2</sub> ratios kept below 2 except for Zr
- 2 mL uranyl sulfate solutions inserted into dry wells during H<sub>2</sub>O irradiations at linac
- Micro-SHINE will be used to test the effects of fission tracks on peroxide formation/destruction

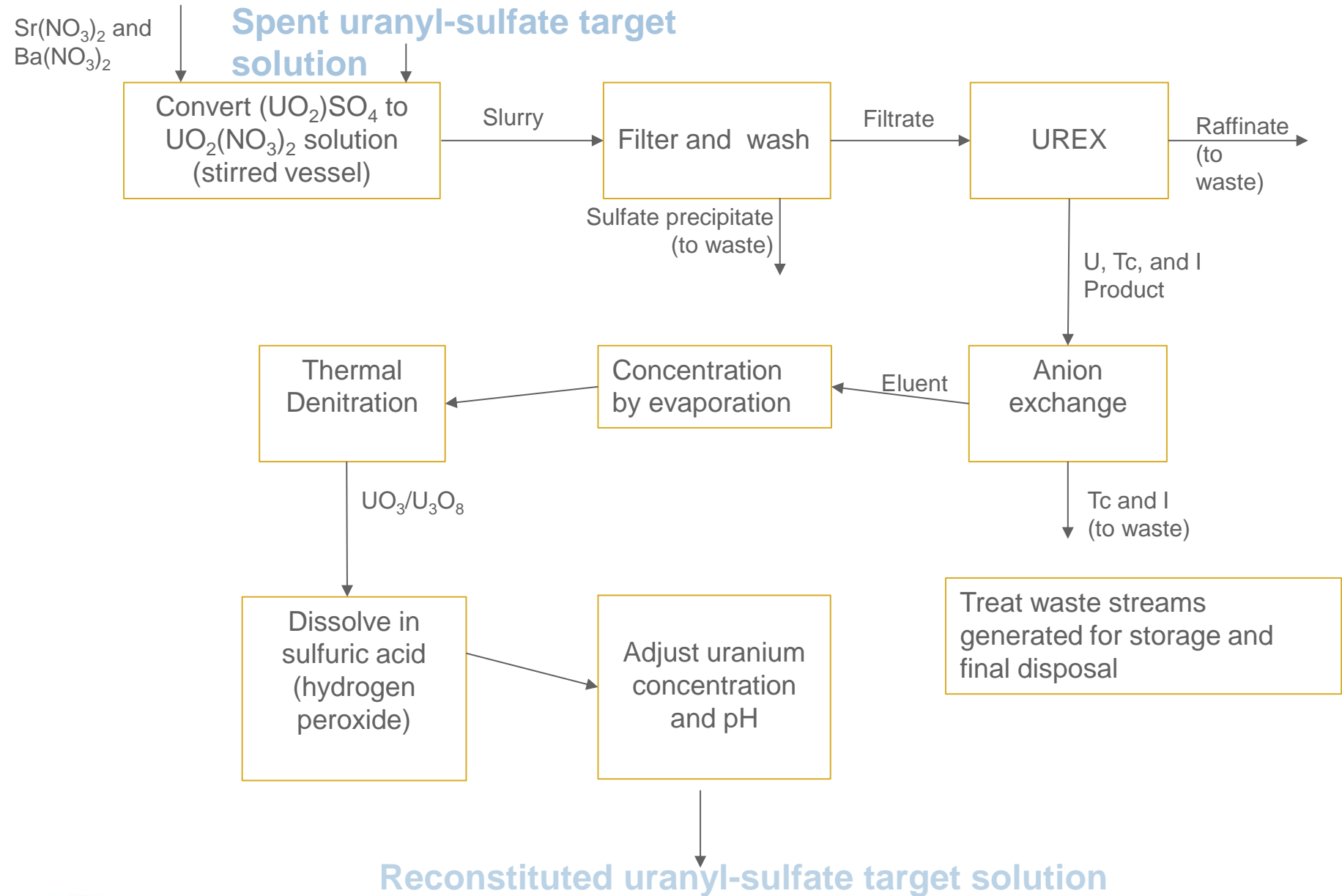


# H<sub>2</sub>:O<sub>2</sub> Ratios with and without Precipitation



- Precipitation occurred for solutions analyzed in top graph
- No precipitation observed for solutions analyzed in bottom graph
- Ratio much larger for samples where precipitation occurred

# Target-Solution-Cleanup Flowsheet



# Sulfate-to-Nitrate Conversion

- Procedure has been developed using a mixture of  $\text{Sr}(\text{NO}_3)_2$  and  $\text{Ba}(\text{NO}_3)_2$  with heat and stirring for nitrate-to-sulfate conversion
- 50 mL uranyl sulfate solution is maximum volume tested and characterized
- A 1.05:1  $\text{Sr}:\text{SO}_4^{2-}$  ratio and 0.05:1  $\text{Ba}:\text{SO}_4^{2-}$  ratio are required to keep Ba below RCRCA levels of 100 mg/L and  $\text{SO}_4^{2-}$  below 0.01 M
- $\text{Sr}(\text{NO}_3)_2$  added first – heated to 60°C with agitation for 30 minutes
- $\text{Ba}(\text{NO}_3)_2$  added next – heated to 60°C with agitation for 60 minutes
- Solution is filtered using a 1 mm Nuclipore filter
- 70 mg/L Ba and 0.005 M  $\text{SO}_4^{2-}$  remain in the filtrate after precipitation



Sr/Ba Sulfate precipitate before rinsing



# Clean-Up with Irradiated DU foils

- 6 g irradiated DU foil used as a spike for a 250-mL uranyl sulfate solution
  - 50 mL was used for nitrate-to-sulfate conversion and UREX batch contacts
  - ~ 1 mCi Mo-99 produced
  - $\gamma, n$  reaction on U-238 to produce U-237 – 1000X more U-237 than other fission products
  - Gamma counting – complex and saturated with U-237
  - Qualitative results rather than quantitative
- 
1. Most if not all of the alkaline earths (Ba and Sr) partition to the precipitate.
  2. Most of the transition metals and iodine partition to the filtrate.
  3. Essentially all of the uranium partitions to the filtrate.
  4. A large fraction of the rare-earth elements partition to the precipitate.
  5. Iodine could not be stripped from organic solvent...mostly I<sub>2</sub>.



# Iodine Removal from UREX Solvent

- ~50% radioiodine partitioned into a 30% TBP/n-dodecane phase from an aqueous phase of 1 M  $\text{HNO}_3$  and  $10^{-6}$  M stable  $\text{I}_2$
- Solvent extraction and liquid chromatography techniques have been utilized to help remove  $\text{I}_2$  from UREX solvent
- Stripping radio-iodine from loaded organic phase proved to be insufficient when using 1 M  $\text{HNO}_3$ ,  $\text{Na}_2\text{CO}_3$ , hydroxylamine, or  $\text{H}_2\text{O}$
- NaOH showed some slight stripping capabilities
- Hydrazine was the most effective at removing iodine but may not be best choice
  - Hydrazine mechanism of action – reduction of  $\text{I}_2$  to  $\text{I}^-$
- Activated charcoal and AMBERCHROM CG116 resin exhibited reasonable separation capabilities as a stationary phase
- More work needs to be done in this area



# Future Clean-Up Experiments

- Future experiments will more closely mimic SHINE conditions
- Stage 2 test will use a small volume of micro-SHINE solution and the solvent-extraction portion will be performed in a centrifugal contactor bank
- More realistic UREX data will be obtained
- Stage 3 test will use irradiated mini-SHINE solution for the clean-up process
- Stage 2 and 3 experiments will provide important data regarding iodine behavior when generated in solution versus in a foil at the linac



# Concluding Remarks

- Plant-scale recovery and concentration columns have been designed and validated on a small-scale
- Low dose rates do not change Mo redox chemistry
- High dose rates lead to the formation and precipitation of uranyl peroxide – catalyst needed to prevent this
- Optimization for Pu removal from titania column is underway
- Procedure for sulfate-to-nitrate conversion has been developed and demonstrated using irradiated DU foils as a spike
- Conversion and UREX tests using centrifugal contactors are planned for solutions spiked with micro-SHINE and mini-SHINE solutions
- Process for iodine removal from UREX solvent is needed – reduction of  $I_2$  to  $I^-$



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